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Angular momentum calculations in coronene mononegative ions

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The orbital angular momentum of some of the π-electron eigenstates of coronene mononegative and dinegative ions were recently calculated with an HMO method.[1] The m.c.d. measurements and some of the conclusions merit further attention. We have done some configuration interaction (CI) calculations for the mononegative ion to check these former preliminary conclusions which are the following:

(a) The $^2E_{1g}$ ground-state orbital angular momentum is well described by the symmetry orbital of the unpaired electron. The effect of CI presumably is very small.

(b) The $^2E_{1g} \rightarrow {}^2A_{1,2u}$ transitions are well interpreted by a simple HMO calculation insofar as the angular momentum is concerned. Again, one might be inclined to assume that CI is not important.

(c) The excited $^2E_{2u}$ states present a problem in that the agreement between calculated and experimentally determined values is rather poor. The use of an orthogonalized set of orbitals leads to an improvement for some parameter values, for others the discrepancies only increase or stay the same.

Using Mataga parameters for the repulsion and exchange integrals a CI calculation for the $^2E_{1g}$ ground state and the $^2A_{1,2u}$ and $^2E_{2u}$ excited states was performed. The number of configurations used for each symmetry was about 50–70 (with increasing energies), however, as one might expect this number is not too critical, higher energies contributing less in general. In view of earlier results the assumption has been made that the ion has D_{6h} symmetry. The β parameter has been adjusted in such a fashion that the transition energies fall within the proper region ($\beta = -1.8$ eV).

In a subsequent calculation the angular momentum for the configurations of interest was calculated in a straightforward way: For each degenerate state the real configurations, which were + or − with respect to reflection in the xz plane, were written as complex conjugate combinations. The angular momentum can finally be expressed in the individual MO contributions each with a factor giving its weight in the configuration.[1]

The results have been collected in Table I. More details of the calculation are also given in the table. The bond lengths were taken equal 1.41 Å and for the Slater orbital parameter (see Ref. 1) $p = 1.625/0.528$ was chosen.

From a comparison with the experimental results we conclude the following:

(a) The ground state of the mononegative ion is well described by the symmetry orbital. CI for this state is very small. The contribution of this orbital to the groundstate is about 0.96, the angular momentum is 1.716 $\hbar$ (as compared to 1.700 $\hbar$ computed previously[1]).

(b) In the region of the m.c.d. measurements one observes[1] two transitions with negative A/D and positive C/D values. These are due to $^2E_{1g} \rightarrow {}^2A_{1u}$, $^2A_{2u}$ transitions. For a parameter value $\beta = -1.80$ eV four transitions with reasonably

TABLE I. Experimental and calculated m.c.d. quantities for coronene mononegative ion. The values calculated according to the PPP method are given in parenthesis. See text.

A.

$^2E_{1g} \rightarrow {}^2A_{1,2u}$ transitions. $A/D^c = -0.858$, $C/D^c = +0.858$

Symm	$\beta = -1.80$ (−1.30) eV		experimental (Ref. 1)			
	ν^a	D^b	ν^a	D^b	A/D^c	C/D^c
$^2A_{1u}$	6.36(9.22)	1.24				
$^2A_{2u}$	11.03(14.64)	0.49				
$^2A_{2u}$	23.97(29.85)	0.69	26.94	0.39	−0.90	+0.60
$^2A_{1u}$	26.96(32.68)	1.38	28.48	0.52	−0.50	+0.60
$^2A_{1u}$	28.84(37.92)	0.63				
$^2A_{2u}$	30.49(39.55)	0.35				
$^2A_{2u}$	38.31	0.09				
$^2A_{1u}$	38.94	0.01				

B.

$^2E_{1g} \rightarrow {}^2E_{2u}$ transitions. $C/D^c = -0.858$

Symm	$\beta = -1.80$ (−1.30) eV			experimental (Ref. 1)			
	ν^a	D^b	A/D^c	ν^a	D^b	A/D^c	C/D^c
$^2E_{2u}$	8.27(10.93)	0.22	+0.108				
	14.06(20.30)	0.61	+2.162				
	21.60(27.16)	0.01	+0.045				
	23.57(32.15)	0.02	+1.110				
	29.33(36.27)	0.94	+1.110	21.10	0.28	+0.73	−0.42
	31.28(40.30)	1.29	+0.193	32.87	1.39	+0.42	−0.24

[a]In kK. [b]In 10^{-16} cm^2. [c]In (Bohr magneton).

large intensities of these types have been calculated (see Table I). For $\beta = -2.40$ eV only two remain within this region, the other ones shift strongly towards the uv. We are therefore inclined to correlate the observed $^2E_{1g} \rightarrow {}^2A_{1,2u}$ transitions at $\nu = 26.94$ kK and 28.48 kK with the transitions $^2E_{1g} \rightarrow {}^2A_{2u}$ at 23.97 kK and $^2E_{1g} \rightarrow {}^2A_{1u}$ at 26.96 kK, respectively. A more negative value than $\beta = 1.80$ eV might be more appropriate.

(c) Restricting our discussion to the value of $\beta = -1.80$ eV two strong and two weak $^2E_{1g} \rightarrow {}^2E_{2u}$ transitions have been calculated within the experimental region. The strong absorptions are located at 29.33 and 31.28 kK, the weak ones at 21.60 and 23.57 kK (see Table I). It therefore seems very possible to assign the two experimentally observed strong absorption bands with $^2E_{2u}$ character (positive A/D and negative C/D) to the bands calculated at 29.33 kK and 31.28 kK. More careful m.c.d. measurements, using a line shape analysis, by Scholtens[2] have revealed the presence of a weak absorption band at about 30.0 kK of the type $^2E_{1g} \rightarrow {}^2E_{2u}$.

Upon taking a more negative value for β the two strong $^2E_{1g} \rightarrow {}^2E_{2u}$ transitions move to higher energies, eventually outside the experimental region.

Although one might argue[1] that vibronic interactions are important, it seems that MO theory in its present form does not provide a certain answer for these transitions.

It may be noticed from Table I that changing β does not lead to a change in order of the $^2E_{1g} \rightarrow {}^2E_u$ transitions.

It is striking that the values A/D are positive in agreement with experiment and contrary to our previous HMO results.[1]

Finally we would like to mention the fact that SCF CI calculations were made with a PPP approximation. The same magnitudes for the energies can be found using a parameter $\beta = -1.3$ eV. The lower energy levels become more crowded than in the other treatment and we therefore prefer the Mataga method which gives better experimental agreement.

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[1]P. J. Zandstra, D. J. Scholtens, and R. E. Koning, J. Chem. Phys. 57, 3821 (1972).
[2]D. J. Scholtens (private communication).